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DEVELOPMENT OF BATTERY SEPARATOR COMPOSITES

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Prepared for:

NASA Lewis Research Center

Cleveland, Ohio 44135

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ABSTRACT

Improved inorganic-organic separators developed by NASA were commercially prepared. A single-ply asbestos substrate was developed, as well as alternative substrates based on cellulose and on polypropylene fibers.

The single-ply asbestos was bound with butyl rubber and was functionally superior to the formerly used polyphenylene oxide saturated sheet. Cellulosic paper and nonwoven polypropylene were both saturated with pigmented mixtures similar to the aqueous barrier coatings.

Solvent-based coatings and aqueous analogs were applied first on laboratory handsheets and then on coating machines. Butyl rubber and thermoplastic rubber emulsions were used as binders for the aqueous coatings.

Commercially prepared separators exhibited better measured separator properties than the NASA standard. Cycle life in Ni/Zn and Ag/Zn cells was related to substrate, decreasing in the order: asbestos > cellulose paper > nonwoven polypropylene. The cycle life of solvent-coated separators was better than aqueous in Ni/Zn cells, while aqueous coatings were better in Ag/Zn cells.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SUMMARY

The commercial preparation of improved inorganic-organic separators for alkaline batteries developed by NASA was undertaken, and is the subject of this report. Development of a single-ply asbestos substrate and of alternative substrates based on cellulose and polypropylene fibers were pursued. Application of solvent-based coatings on these substrates, and development and application of aqueous barrier coatings were also achieved.

A fuel cell grade asbestos sheet was made on a cylinder machine, using a butyl rubber emulsion as the binder. This base was functionally superior to the formerly used asbestos sheet which was saturated with polyphenylene oxide. A cellulose base paper saturated with pigmented systems similar to the NASA coatings proved to be a suitable coating base with good porosity. Nonwoven polypropylene webs treated to make them wettable also were made and barrier coated.

NASA solvent-based coatings were applied on continuous coating machinery. The original K19W1 formulation coated well, but produced separators with high electrical resistance. Formulations with improved low resistance, typified by K158, required great care in application to minimize the tendency to form cracks during drying. High proportions of very fine particle size pigments appear to be the cause of the cracking.

Aqueous analogs of the solvent-based coatings were also evaluated, using butyl rubber latex as the binder. This made low cost coatings which provided barrier properties similar to the solvent coatings. The particular emulsion binder used most extensively, for economic reasons, did cause blocking problems because of its softness and flow characteristics. Thermoplastic rubber, which combined oxidation resistance and low blocking tendency was not available in emulsion form. Solutions of thermoplastic rubber were successfully emulsified and compounded. Colloidal problems, now believed to be solved, restricted machine coating work to short yardages.

Commercially-prepared separator materials behaved in the following manner:

1) Measured separator properties, particularly resistivity, were improved when compared to the NASA solvent-based separators.

2) Limited NASA testing of barrier separators showed better cycle life in nickel-zinc cells when barrier coatings were on asbestos rather than cellulose or polypropylene. Nevertheless, the Kimberly-Clark permanently wettable propylene absorber separator used as a coating base for the above (when used as an absorber only), showed cell lives in excess of 6,000 cycles during one and one-half years of testing in nickel-cadmium cells.

3) Solvent-based coating showed better cycle life than aqueous coatings in nickel-zinc cells, while aqueous coatings were better in silver-zinc cells.

INTRODUCTION

A research program to develop improved alkaline batteries was undertaken by NASA Lewis Research Center in 1973. One aspect of this program was concerned with an inorganic-organic (I/O) separator system originally described in a patent issued to Astropower Corporation (Ref. 1). The separator was designed to prevent zinc dendrite penetration through the separator, the dendrites being the primary cause of internal electrical shorts in secondary alkaline zinc systems. NASA improved the flexibility of these separators by reformulating the dendrite barrier coatings and utilized a thermoplastic elastomer as the primary binder (Ref. 2). In addition, improvements in the available asbestos substrates for these coatings were needed, both in uniformity and cost. This coupled with the increasing concern over the hazards of asbestos led to a search for other substrates as carriers for dendrite barrier coatings. Another area demanding improvement was the coating compositions, many of which contained chlorinated solvents. The relatively heavy coatings led to vapor emissions which exceed government restrictions, in addition to introducing high costs.

The Munising Paper Division of Kimberly-Clark (now called Munising Paper Company, a Division of Kimberly-Clark Corporation), specialists in saturated and coated papers, was awarded Contract NAS3-20583 to attack these problems. One primary objective of this contract was to develop other substrates as a replacement for asbestos to carry dendrite barrier coatings. Another was to modify the solvent-based separator coating formulations for compatibility with aqueous systems. Another goal was to assist in the development of dendrite barrier separator composites for alkaline battery cells having improved cycle life and performance characteristics. Secondary goals of the contract were to improve the quality of the asbestos substrate and to demonstrate commercial production feasibility of solvent-based separators.

The work was divided into five tasks originally, and expanded to six in Modification I dated November 30, 1977. The tasks were as follows after Modification I was introduced:

Task I	Filled Cellulose Fiber, Mineral Fiber and Polyolefin Fiber Webs
Task II	Coating Systems
Task III	Foam and Microcellular Coatings (deleted in its entirety under Modification I)

Task IV Calendering (Incorporated in the process for Tasks I-II)

Task V Establishing Optimum Processing Capability for Separators

Task VI Reporting Requirements

Task VII Quality Assurance

The vast majority of the work was done under Tasks I, II, and V. The experimental work is therefore reported here under subject headings based on these tasks. Development of substrates and coatings for the substrates were the two major areas of effort. Because a fairly large number of different coatings were evaluated, the coatings are subdivided into solvent and aqueous variations.

Most of the electrical evaluation of the experimental separators was done at the Lewis Research Center. All test cells were prepared and cycled by NASA. Results of test cells reported here were provided by NASA.

RESULTS AND DISCUSSION OF RESULTS

I. Substrate Design

A. Asbestos Sheets

The asbestos base sheet used by NASA at the time this contract was initiated was made on a cylinder machine from four plies of fuel cell grade asbestos. Cylinder machines are paper machines which form a web against a cylinder covered with a wire screen, and carrying a partial vacuum to speed the flow of water through the wire from a pulp slurry. Generally webs are formed on several such cylinders and joined while wet to form heavier sheets (See Ref. 3). No binder was used, and the sheet was extremely weak. In order to improve the strength to make coating possible, the four-ply sheet was saturated with 2% polyphenylene oxide (PPO) from solvent. The PPO was found to be concentrated near the surfaces of the sheet, which is characteristic for thick sheets impregnated with resins in solution. As a result of this migration to the sheet surfaces, little binder remained at the interface between plies. There was a strong tendency for ply separation when this asbestos sheet was immersed in electrolyte.

To overcome the weakness of multi-ply asbestos sheets, a program was undertaken to make 7-mil (0.18 mm) asbestos sheet in a single ply. An additional goal was elimination of the costly impregnation step. For many years asbestos sheets have been made with rubber latex binders added to the water-dispersed pulp before sheet formation (Ref. 4). The reactive nature of the asbestos fiber surface allows the easy deposition of many latex polymers, even at high dilution. When binders are applied to fibers in this way, there is no migration problem, even when very thick sheets are formed.

To choose a binder for asbestos separators, a prime consideration is the resistance to oxidation in concentrated potassium hydroxide solutions. Most elastomers contain many olefinic bonds and have poor oxidation resistance as a result. Of the relatively few saturated rubbery polymers, butyl rubber was chosen as the best candidate because it was available commercially in emulsion form and at a reasonable price. The particular butyl rubber which was available as an emulsion was rather soft and led to sticking problems on the forming wire. The level of binder concentration was held to 5% of the fiber weight to reduce this tendency.

The initial handsheets were prepared with a fuel cell grade of chrysotile asbestos. The pulp was dispersed in a gallon size Waring blender using 5 grams of asbestos in 300 ml. of water. After the pulp was fiberized, 0.125 grams of Tamol 731 dispersant solids were added, followed by 0.25 grams of Butyl Latex 100 (BL-100) solids. The composition of these materials and their manufacturers are given in Table I, along with all the other commercial products used in this project. Drainage in the sheet mold was speeded by using vacuum. Sheets were pressed between blotters at 125 psi (0.86 MPa) while still on the wire, then stripped and dried on a steam-heated drum.

Work done with the handsheets of beater-treated asbestos (BTA) was successful enough to warrant a production trial. The trial was made on a cylinder machine at Quin-T Corporation, using only a single mold to avoid weakness along ply lines. The fiber used was fuel cell chrysotile which had previously been processed into sheet form. It had already been refined, and contained adequate dispersant so that further additions were not desirable. (A working supply of single-ply BTA was successfully manufactured, totaling approximately 1300 square yards.) In the operation of the cylinder machine there was necessarily a great deal of pumping, spraying, and cascading of the pulp slurry. The butyl latex, which was preferred because of the chemical resistance of the polymer, had a tendency to foam. The foam led to some loss of uniformity in sheet formation and strength.

A similar production trial was made using a lower cost electrical grade of asbestos fiber, Paperbestos #5. Because cell tests with handsheets made from electrical grade pulp gave inferior results, the production trial sheet was not utilized in pilot coating runs. Physical properties of the production sheets are listed in Table II measured by TAPPI standard tests.

Two commercially available asbestos sheets from Manning Paper Company were also evaluated in pilot coating work. Both grades, Mannitemp 111 and Mannitemp 172, were made with electrical grade chrysotile. Mannitemp 111 contained some glass fiber and Mannitemp 172 contained some cellulose fiber, and both used an acrylic binder. These sheets had good strength. In addition to the oxidizable cellulose and acrylic binder, the electrical grade asbestos introduced about twice as much iron as the fuel cell grade asbestos. These products are no longer available because of health hazards associated with asbestos.

TABLE I. COMMERCIAL PRODUCTS UTILIZED IN SEPARATORS

Trade Name	Composition	Manufacturer
Tamol 731	Sodium Salt of a Carboxylate Polyelectrolyte	Rohm & Haas Company, Philadelphia, PA 19105
Butyl Latex 100	Butyl rubber emulsion	Burke-Palmason Chemical Co.,Pompano Beach,FL 33060
Mannitemp 111	Asbestos Paper	Manning Paper Company, Troy, NY 12181
Mannitemp 172	Asbestos Paper	Manning Paper Company, Troy, NY 12181
Meltblown Polypropylene	Polypropylene Nonwovens	Kimberly-Clark Corporation, Neenah, WI 54956
SWP Synthetic Wood Pulp	High Density Polyethylene Fiber	Crown Zellerbach Corp., San Francisco, CA 94119
Kraton	Thermoplastic Rubber	Shell Chemical Company, Houston, TX 77002
PPO	Polyphenylene Oxide	General Electric Company, Selkirk, NY 12158
Paraplex G62	Epoxidized Soybean Oil	Rohm & Haas Co., Philadelphia, PA 19105
Plastolein 9750	Polymeric Plasticizer	Emery Industries, Cincinnati, OH 45202
Cab-O-Sil M5	Fumed Silicon Dioxide	Cabot Corporation, Boston, MA 02110
Ticon PT	Lead Titanate	NL Industries, Hightstown, NJ 08520
Wollastonite P-15	Natural Calcium Silicate	Interpace Corporation, Willsboro, NY 12996
Ticon MT	Magnesium Titanate	NL Industries, Hightstown, NJ 08520
Ticon CZ	Calcium Zirconate	NL Industries, Hightstown, NJ 08520
Hydrite UF	Kaolin Clay	Georgia Kaolin, Elizabeth, NJ 07207
Unitane 0-110	Titanium Dioxide	American Cyanamid Co., Organic Chemicals Division, Bound Brook, NJ 08805
P-25 Titanium Dioxide	Titanium Dioxide	Degussa Corporation, Teterboro, NJ 07608
Rhoplex HA16	Polyacrylate Emulsion	Rohm & Haas Company, Philadelphia, PA 19105
Wood Flour	100 Mesh White Pine	Wood Flour, Inc., Winchester, NH 03470
Ticon LZT	Lead Zirconium Titanate	NL Industries, Hightstown, NJ 08520
Ticon CZS	Calcium Zirconium Silicate	NL Industries, Hightstown, NJ 08520
Arkon P-85	Alicyclic Hydrocarbon Resin	Arakawa Chemical Industries, Ltd. Osaka 541, Japan
Rhoplex B15	Polyacrylate Emulsion	Rohm & Haas Company, Philadelphia, PA 19105
Surlyn 56230	Ionomer Dispersion	E. I. Dupont de Nemours & Co., Wilmington, DE 19898
Nyad 400	Natural Calcium Silicate	Interpace Corporation, Willsboro, NY 12996
Carbopol 940	Polyacrylate Thickener	B. F. Goodrich Chemical Co., Cleveland, OH 44131
Igepal CO-887	Nonionic Surfactant	GAF Corporation, New York, NY 10020
Elvanol 71-30	Polyvinyl Alcohol	E. I. Dupont de Nemours & Co., Wilmington, DE 19898
Gulf PA-18	Octadecene-1/Maleic Anhydride Copolymer	Gulf Oil Chemicals Company, Houston, TX 77001
Strodex PK-90	Organic Polyphosphoric Ester Surfactant	Dexter Chemical Corporation, Bronx, NY 10474
Ultrawhite 90	Kaolin Clay	Engelhard Minerals & Chemicals Corp., Edison, NJ 08817
Surlyn 56220	Ionomer Dispersion	E. I. Dupont de Nemours & Co., Wilmington, DE 19898

TABLE II. PHYSICAL PROPERTIES OF BEATER-TREATED ASBESTOS

			7-mil Fuel Cell Grade	5-mil Paperbestos
Basis Weight g/m^2			135.7	99.0
Caliper, mm (mils)			0.17 (6.8)	0.11 (4.5)
Tensile Strength	MD[1]	kN/m (lbs./in.)	0.30 (1.7)	0.26 (1.5)
	CD[2]	kN/m (lbs./in.)	0.25 (1.4)	0.26 (1.5)
Elmendorf Tear	MD	g/16 sheets	10.8	9.6
	CD	g/16 sheets	12	10
Elongation	MD %		1.1	5.2
	CD %		1.5	6.2

[1] Machine direction samples are cut so that the tensile stress is applied parallel to the direction of continuous travel of the forming web on a paper machine.

[2] Cross direction samples are cut at right angles to machine direction.

In handsheet work on substrates several other fiber combinations were examined. Blends of synthetic wood pulp (high density polyethylene in water dispersible fiber form) with asbestos and with cellulose (wood pulp) were made into handsheets. The synthetic wood pulp offered the possibility of heat bonding without further treatment other than calendering. The water repellency of the fused fibers led to poorer wetting of the bonded sheets and higher electrical resistivity. No work was done with these combinations beyond the handsheet stage.

B. Cellulosic Papers

The health hazards of asbestos have become well recognized in recent years, so much so that strict government regulations have been established to govern its use (Ref. 5). As a result, there is an increasing unwillingness to manufacture or to use products containing asbestos. There was a need for alternative substrates to be developed for separators. One possibility was cellulose papers saturated with suitable emulsion polymers. Saturating grade papers generally have an open structure to allow the absorption of large amounts of impregnants, and are thus rather porous even after saturation. This allowed good electrolyte holding power and yet provided a good coating base for barrier type coatings. The same formulations used for barrier coatings of the type utilized in the inorganic-organic separator design were adapted to use as saturants. It was necessary to use a rubbery or soft plastic binder in order to have adequate tear resistance for handling and fabrication into finished separators. A production run of this type of substrate, No. S-47971, was made from a bleached kraft base paper saturated with approximately 28 parts of a pigmented butyl latex formulation per 100 parts of fiber. Physical properties of S-47971 are listed in Table III.

C. Polypropylene Nonwovens

A second area of potential replacements for asbestos is comprised of nonwoven fabrics made from alkali and oxidation-resistant fibers of textile length. Such fabrics have already been applied in many separator applications. The type on which Kimberly-Clark has concentrated was based on nonwoven polypropylene (Ref. 6). Polypropylene has excellent chemical resistance, but it is a difficult material to wet with water, and even more so with alkaline aqueous

TABLE III. PROPERTIES AND FORMULATION OF S-47971

PROPERTIES

Item	Basis Wt. g/m^2	Caliper cm (mils)	8 Sheet Gurley Porosity Seconds/100 cc	MD Dry Tensile kN/m (lbs./in.)	MD Dry Elongation %	MD Elmendorf Tear g/16 sheets
BASE PAPER	62.0	0.017 (6.5)	8.8	-	-	-
S-47971	85.7	0.018 (6.9)	12.7	3.3 (18.6)	3.1	166

FORMULATION

BASE PAPER: Bleached saturating kraft wood pulp

S-47971: Saturated* BASE PAPER

			Dry Parts by Wt.
* Saturant:	Pigment Dispersion	Tamol 731	1
		Nyad 400	100
	Binder	BL-100	50

electrolytes. Preliminary efforts to modify the polypropylene fiber surfaces to make them wettable showed that pigmented formulations like the I/O barrier coatings were not effective. Two separate wetting problems needed solution. The first was the difficulty of completely wetting a polypropylene web with a dilute aqueous impregnant. The second problem was to find additives which would later serve to make the dry sheet readily wettable with electrolyte. Many types of surfactants were effective in providing easy saturation. However, most of the surfactants which were useful for the saturation step were not effective in rewetting with concentrated KOH solution.

One class of surfactants which was found to be especially effective for rewetting dry separator materials with KOH electrolyte was the phosphate ester type. Levels of surfactant of about one percent on the fiber weight provided good wettability. After these pigmented formulations containing the required surfactant had been wetted with electrolyte they remained wet indefinitely. This was not true of just the polypropylene fibrous webs treated with the same surfactant alone; such wettable webs actually dewetted even while immersed in electrolyte.

Initially, the pigmented formulations used to develop wettability in polypropylene utilized the pigment systems of the NASA barrier coatings. Lower cost pigments, such as calcium silicate and kaolin clay, were later used exclusively. The lower cost systems were equally effective in providing wettability. The electrolyte holding power was high because of the very open structure, just as it is for other nonwoven fabrics. This structure made it necessary to use special precautions in coating to prevent coating penetration.

Selected test values for production runs of the various types of substrate are listed in Table IV.

TABLE IV. SELECTED SEPARATOR TESTS FOR SUBSTRATE TYPES[1]

Substrate	Basis Weight g/m^2	Dry Caliper cm	Wet Caliper cm	Bubble Pressure[2] kPa	Maximum Pore Diameter[3] μ m	Electrolyte Absorption[4] %	Volume Resistivity[4] Ω cm
PPO treated asbestos	253	0.028	0.030	24	9.2	114	15.6
BTA	143	0.019	0.022	Ruptured at 21	-	302	2.7
S-47971 (Cellulose)	83	0.015	0.047	5.7	40.9	592	2.5
S-49024 (Polypropylene)	53	0.025	0.025	4.4	53.8	755	0.32

[1] Tests run at Kimberly-Clark.

[2] Kimberly-Clark test apparatus and method, similar to ASTM Method E-128; sample backed by aluminum window screen.

[3] Calculated from bubble pressure.

[4] Air Force Aero Propulsion Laboratory Screening Method (Ref.10).

II. Solvent-Based NASA Coatings

Four solvent-based coatings studied extensively by NASA were chosen for the initial coating work. They were representative of the original Astropower coatings and NASA modifications. Their formulations are given in Table V. One objective of the contract was to demonstrate the commercial application of solvent-base coatings on selected substrates. The PPO coatings presented extreme difficulties because of the chloroform solvent. The rapid drying caused skin formation on the chloroform coating, and worker exposure to chloroform vapors around compounding and coating equipment would be excessive. These factors and the undesirable brittleness of the coating led to the decision not to make pilot coatings with chloroform solutions. The more flexible K19W1 and K19W2 were therefore the solvent coatings of choice.

The initial pilot coating trials were run on a 24-inch Faustel coater-laminator using 7-mil BTA as the substrate (See Section IA). To successfully coat the low strength BTA with K19W1 a carrier web was required. The preferred method would be with a belt through the coater. The coating method used was "nip-fed reverse roll." For a description of this coating arrangement, as well as the other coating methods used in this work, see Reference 7. The coating weight of 134 g/m^2 was applied in two coats. The application in two coats was specified by NASA since lab work indicated superior results over single coats of the same total weight. Double-coating would be expected to reduce the possibility of flaws which extend through the entire thickness of the coating. The volume resistivity of the K19W1 coated BTA was higher than desirable. Some of the coating mixture used in the trial was applied to some of the same BTA in the laboratory in six successive coatings. This produced coat weights ranging from 35 to 168 g/m^2. Resistivities were measured for each of these and were found to rise almost linearly after a minimum coat weight of 60 g/m^2 was reached (cf. Fig. 1). All resistivities reported here were measured by the direct current method after heating the samples for 16 hours at 90° C in 45% KOH. The heat treatment was necessary to develop lower resistance by the reaction of the plasticizer in the coating. The high resistivities of K19W1 on BTA were in conflict with results from earlier coating work by NASA.

Coatings of the same K19W1 used above were applied at NASA and the volume resistivity was nearly constant in the coat weight range from 72 to 128 g/m^2. Laboratory work to reconcile differences in resistance between NASA coated sheets

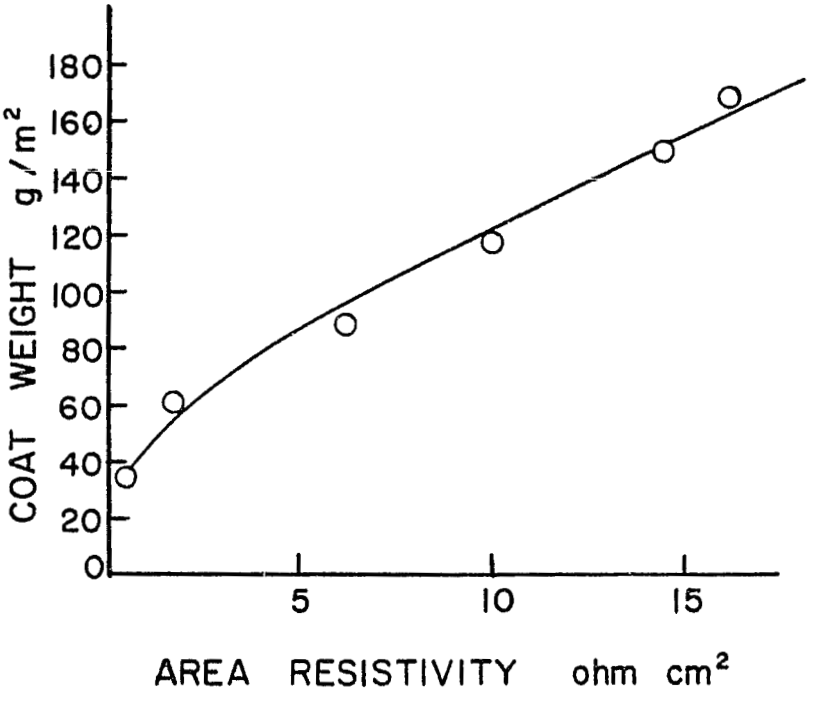
TABLE V. SOLVENT-BASED NASA COATING FORMULATIONS [1]

	K19W1	K19W2	X40	X47 W1
Kraton GX7050	40	40	-	-
Trichloroethylene	500	500	-	-
PPO	-	-	47	47
Chloroform	-	-	410	410
Paraplex G62	16	16	-	-
Plastolein 9750	-	-	47	47
Cab-O-Sil	3.2	6.4	4.8	2
Lead Titanate	20	20	-	-
Wollastonite P-15	55.2	55.2	-	26.2
Magnesium Titanate	-	-	-	36
Calcium Zirconate	-	-	142	-

[1] Parts by weight.

FIGURE 1

EFFECT OF COAT WEIGHT OF K19WI ON AREA RESISTIVITY



and those coated at Kimberly-Clark showed that major differences were produced by variations in drying conditions. K19W1 was applied in two successive coatings, the first at 11 wet mils and the second at 9 wet mils, using a lab knife-over-roll coating arrangement. Drying conditions were varied and the resistances measured as listed in Table VI. These results explained some of the differences between earlier results, since the earlier coatings (even production trials) made by NASA were dried without using heat in the ovens. Drying at room temperature is a costly limitation when coatings as heavy as these ($\cong$60 g/m^2 dry) are applied commercially. Nevertheless, a machine coating was made with no heat in the ovens. Even this run showed substantially higher resistivity than sheets dried with no forced air circulation. Good air circulation is essential on coating machines to vent the organic solvents safely, unlike drying small samples in a laboratory. The components of this solvent coating must have been distributed in different ways depending on drying condition. This is not surprising in view of the solubility characteristics of Kraton. Paraplex G-62, the component responsible for lowering the resistivity, is a nonsolvent for Kraton, and would be expected to throw the Kraton out of solution to varying degrees at different temperatures and concentrations.

Handsheet samples of K19W2 on BTA (designated K19W2G and similar to K19W1) gave comparable cycle life as an earlier production control of K19W1, but provided better capacity retention. The control was coated at Duracote Corporation by NASA. Cell testing was in 8 amp-hour Ni/Zn cells at 50% depth of discharge (DOD) and carried out according to NASA procedures as indicated in the Appendix. Test results are summarized in Fig. 2.

During the course of this contract promising new solvent coatings were developed at NASA. These new formulations had much lower resistance than K19W1. One such formulation, which was studied extensively and coded K158, is given in Table VII. This coating was characterized by containing large amounts of ultra fine particle size pigments, particularly the P-25 titanium dioxide. Another important change from K19W1 was substitution of Plastolein 9750 for Paraplex. This latter change reduced resistance in many formulations. The Kraton was also a different grade, which was more easily soluble than the higher molecular weight Kraton GX7050. Unfortunately, the changes to ultrafine pigments in K158 and similar variations resulted in a tendency to develop coating cracks during drying. Changes in solvent composition helped reduce cracking, and application of

TABLE VI. VARIATION OF RESISTIVITY WITH DRYING CONDITIONS

	Coat Weight g/m^2	Area Resistivity ohm cm^2
Both coats dried at room temperature	125	1.52
Both coats dried in lab oven at 105^{o} C.	129	4.19
Both coats dried with a lab heat gun	126	5.13

FIGURE 2

CYCLE LIFE COMPARISONS IN NICKEL–ZINC CELLS

8 HOUR CYCLE – 50% DOD – C/4 DISCHARGE RATE

* POINT AT WHICH VOLTAGE AT END OF DISCHARGE DROPPED BELOW 1 VOLT

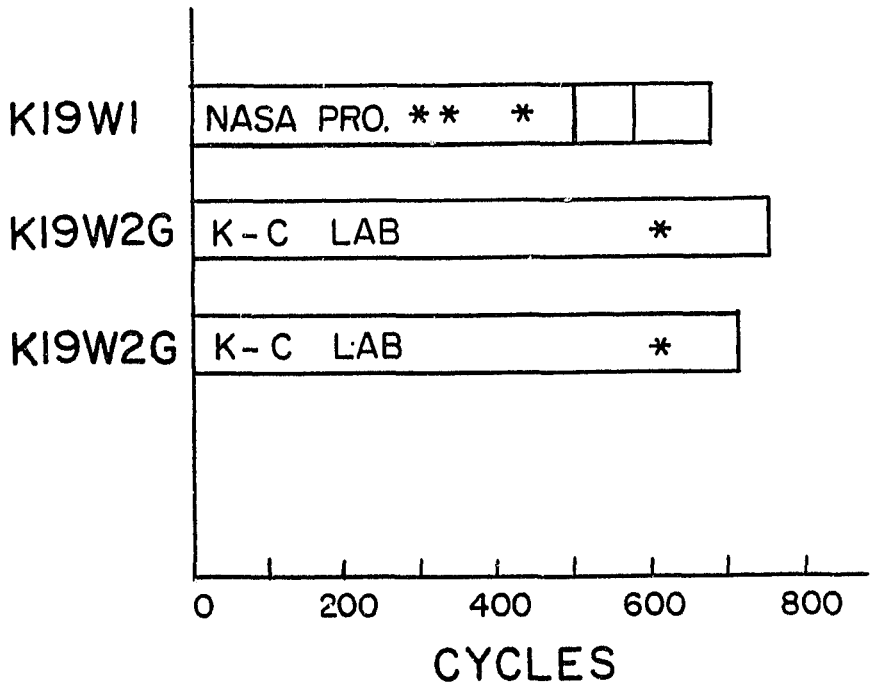


TABLE VII. K158 FORMULATION[1]

Kraton G1650	40
Toluene	300
Plastolein 9750	20
Hydrite UF	26.3
Unitane O-110	36
Lead Titanate	22.5
P-25 Titanium Dioxide	16

[1] Parts by weight.

multiple coatings helped considerably. By using four or five separate coats, good quality handsheets were prepared in the laboratory for evaluation in cells. The initial pilot coating runs with K158 were not satisfactory because of crack formation. The second coat caused cracks to develop in the first coat even before the sheet entered the oven. In a second trial, using no heat in the oven, flaws were reduced in number but still present. The only way to completely overcome the problem was to use higher levels of Kraton binder, which predictably resulted in excessively high electrical resistance.

Modifications of the design K158 were developed at NASA and handsheets prepared at Kimberly-Clark for evaluation. Formulations are given in Table VIII and are at equivalent ratios of binder-to-pigment volume concentrations. The coatings were applied in multiple coats to minimize cracking. All of the coatings were dried at room temperature. The formulations utilizing wood flour in place of inorganic pigment have a more favorable ratio of binder-to-pigment surface area because of the larger particle size of the wood flour. As a result they are more resistant to coating cracks. The wood flour leads to a rough textured surface and causes spreading problems with some coating methods which favor separation of larger particles during the metering of wet coating. In this case, reverse roll coating is a satisfactory coating method.

Two of the wood flour coatings also contain an acrylate polymer in emulsion form in place of Paraplex or Plastolein. The use of these acrylate emulsions is discussed under aqueous coatings, in which they are particularly useful in lowering resistance. The emulsion mixed smoothly into the toluene-based coatings in spite of its water content.

The test results for these handsheet samples are listed in Table IX. The samples had low resistance, and some showed promise in cycle life.

Four modifications of K158 were chosen for pilot coating (cf. Table X). The solvent coatings made previously were prepared by ball milling. These four coatings, and the wood flour coatings above, were prepared in a Segvari attritor, which is faster and more practical for preparing the quantities of coating needed. These coatings were applied on a Faustel pilot coater. This was a 14-inch coater equipped with a long tunnel oven, allowing high drying capacity with good temperature control.

TABLE VIII. MODIFIED K158 TYPE COATING FORMULATIONS[1]

	K169	K172	K173	K174	K164T	K166T	K168T	K143B	K143C	K143D
Kraton G-1650	40	40	40	32	40	40	40	40	40	40
Toluene	350	350	350	265	350	350	350	350	350	350
Paraplex G62	16	-	-	-	-	-	-	-	-	-
Calcium Zirconium Silicate	116.3	116.3	-	-	-	-	-	-	-	-
Cab-O-Sil M5	4.8	-	-	-	-	-	-	4.8	-	4.8
Plastolein 9750	-	16	16	12.8	20	-	20	-	-	16
P-25 TiO_2	-	20	20	16	16	16	16	-	20	-
Wood Flour	-	-	24	-	-	-	-	24	24	24
Lead Zirconium Titanate	-	-	-	166.4	-	-	15.2	-	-	-
Hydrite UF	-	-	-	-	26.3	26.3	26.3	-	-	-
Unitane O-110	-	-	-	-	36	36	36	-	-	-
Magnesium Titanate	-	-	-	-	-	10.1	-	-	-	-
Rhoplex HA-16 (wet)	-	-	-	-	-	-	-	35.2	35.2	-

[1] Parts by weight.

TABLE IX. STANDARD SEPARATOR TEST RESULTS
SOLVENT-COATED LABORATORY HANDSHEETS[1]

Coating	Substrate	Dry Thickness cm	Volume Resistivity Ω cm	Porosity %	Zinc Diffusion Rate mol/cm^2 min ($X 10^7$)	Zinc Penetration cm/min ($X 10^4$)	Pore Radius o A	Cycle Life[2] To < 1 Volt at End of Discharge			Cycle Life[2] To < 40% of Capacity at > 1 Volt		
K169	BTA	0.0260	70	50	1.45	2.7	104	274	46	254	341	479	390
K172	BTA	0.0254	21	58	2.76	3.4	114	262	204	17	285	355	543
K173	BTA	0.0254	33	56	1.35	3.1	67	113	273	271	428	372	316
K174	BTA	0.0267	25	51	1.24	2.5	98	203	179	149	340	385	203
K164T	BTA	0.0254	20	52	3.0	2.5	74	341	293	320	435	429	415
K166T	BTA	0.0260	16	53	0.72	2.8	93	356	111	271	443	420	289
K168T	BTA	0.0257	19	54	6.0	2.6	69	403	436	389	519	540	402
K143B	BTA	0.0529	5.9	57	0.14	10.0	57	292	112	-	386	277	-
K143C	BTA	0.0318	13	60	1.3	5.1	49	293	289	124	351	356	480
K143D	BTA	0.0269	15	59	9.5	5.7	1850	194	292	182	194	322	349

[1] All tests done at NASA using NASA Screening Test Procedures.

[2] Nickel-zinc cells - 8-hour cycle - 50% DOD - C/4 Discharge Rate

TABLE X. K158 VARIATIONS FOR MACHINE COATING [1]

	K168T	K172	K173	K177
Kraton G1650	40	40	40	40
Plastolein 9750	20	16	16	20
Toluene	350	350	350	350
Hydrite UF	26.3	-	-	26.3
Unitane O-110	36	-	-	36
P-25 TiO_2	16	20	20	16
Lead Zirconium Titanate	15.2	-	-	-
Calcium Zirconium Silicate	-	116.3	-	12.9
Wood Flour	-	-	24	-

[1] Parts by weight.

Each of these coatings was spread satisfactorily by a pan-fed reverse roll method. A saturated cellulosic sheet, wettable polypropylene webs, and BTA were coated. On each of these substrates all four coatings spread smoothly, but the dried coatings all developed cracks which would destroy their effectiveness as a barrier. Just as with K158, it appeared that the high modulus Kraton binder is not stretchable enough at the high pigment-to-binder ratio of these coatings. The cracking was more extreme on cellulose sheets than on polypropylene or asbestos, no doubt because dimensional changes in going from oven-dried to humid air were greater on cellulose. In fact, coated paper samples taken directly from the oven were observed developing cracks as the moisture content increased. Changes in drying conditions and application of multiple lighter coatings helped to a degree, but did not eliminate the cracking. Addition of resins which had a plasticizing action on Kraton did greatly reduce the cracking tendency. Each of the coatings on Table VIII were modified by substitution of Arkon P-85, a hydrocarbon resin which is fully saturated, for half of the Kraton 1650 in the recipes. All of the coated sheets were made by reverse roll coating, and represent the best coating uniformity achievable without increasing the binder level.

Formulation K172 was applied to BTA and to Type S-47971 cellulosic base, both with and without the substitution of Arkon for half the Kraton. Resistance of the plasticized samples was markedly lower on both the asbestos and cellulosic substrates. Zinc diffusion rate and pore size were higher for the plasticized coating on BTA, and the electrolyte absorption was lower. All these differences may have resulted from a greater degree of coating penetration by the plasticized coating. The plasticizer gave a lower viscosity at the same solids, which favored penetration of the wet coating. The rate of capacity loss on cycling Ni-Zn cells was approximately 20% greater with the plasticized coating. Arkon modified coatings are identified in Table XI by a "P" in the coating identification column.

Extra yardage of K168 on BTA was prepared for use in a wheelchair battery application. Cracks were still present in the second coat, but a dye solution in isopropanol brushed on the coating did not show penetration. The dye highlights the bubbles and cracks, but they do not extend through the entire coating thickness. Furthermore, the zinc diffusion rate remains low, so the coating appears to be a good barrier. Figure 3 shows the magnitude of the cracks.

TABLE XI. STANDARD SEPARATOR TEST RESULTS
PILOT AND PRODUCTION COATED MATERIAL[1]

	Coating		Substrate	Dry Thickness cm	Volume Resistivity Ω cm	Porosity %	Bubble Pressure (H_2O) kPa	Zinc Diffusion Rate mol/cm²min (X 10^7)	Zinc Penetration cm/min (X 10^4)	Pore Radius Å	Cycle Life[2] To < 1 Volt at End of Discharge			Mean (1 Std. Dev.)	Mean[6] X1.8
	K19W1	S[3]	PPO treated asbestos	0.030	40	65	-	-	5.5	120	250	255	260	252 ± 10	
	K19W1	S	BTA	0.025	33	62	-	-	8.7	195	137	-	188		
	K19W1	S	Mannitemp 111	0.026	64	43	-	-	18.9	134	376	350	367	364 ± 13	
	K158	S	Mannitemp 111	0.026	28	55	-	-	1.1	54	241	220	104	231 ± 35	
	K158	S	Mannitemp 172	0.028	22	55	-	-	6.9	23	256	106	207	231 ± 35	
*	K168P	S	BTA	0.022	6.9	63	117	5.1	10.8	100	82	147	175	161 ± 20	290
*	K168P	S	Cellulose Paper	0.022	3.2	42	> 345	3.6	12.8	211	46	119	53		
*	K168P	S	45 g/m² PP Nonwoven	0.032	13	19	> 345	7.1	8.4	138	69	86	71		
*	K168P[4]	S	BTA	0.022	5.6	66	18	0.4	7.6	98	209	233	226	222 ± 12	400
*	K172	S	BTA	0.023	22	50	34	2.2	3.5	43	213	165	196	191 ± 24	344
*	K172P	S	BTA	0.022	8.0	60	21	4.4	11	71	167	162	71	164 ± 4	296
*	K172	S	Cellulose Paper	0.022	15	45	21	5.6	7.4	153	23	162	169	165 ± 5	298
*	K172P	S	Cellulose Paper	0.021	5.2	45	21	5.4	13	128	160	125	89		
*	K172P	S	45 g/m² PP Nonwoven	0.033	19	22	21	4.3	7.3	120	47	76	46		
*	K173P	S	BTA	0.029	12	54	69	3.3	6.0	75	176	23	48		
*	K173P	S	Cellulose Paper	0.031	11	49	21	4.8	34	238	156	69	44		
*	K173P	S	45 g/m² PP Nonwoven	0.048	27	26	76	1.5	5.2	92	24	45	161		
*	K177TP	S	BTA	0.022	5.9	55	21	8.3	4.3	55	160	153	165	159 ± 6	287
*	K177TP	S	Cellulose Paper	0.022	6.4	53	28	2.9	7.1	108	142	161	166	156 ± 12	281
*	K177TP	S	45 g/m² PP Nonwoven	0.036	14	17	21	3.7	5.7	126	99	161	144	152 ± 12	274
	K40A	A[5]	Cellulose Paper	0.018	13	26	-	-	13.4	11430	231	99	222	226 ± 6	
	K40	A	BTA	0.021	15	52	-	-	9.2	780	253	216	223	230 ± 20	
	K40C	A	Mannitemp 111	0.025	14	60	-	-	15.3	133	260	260	209	243 ± 29	
*	K172	A	BTA	0.024	6.8	53	222	3.1	8.8	128	126	153	130	136 ± 15	245
*	K172	A	45 g/m² PP Nonwoven	0.036	8.7	19	182	11.3	11.3	303	59	64	86		
*	Nyad ctg	A	Cellulosic Paper	0.025	6.0	34	65	8.4	10.2	607	75	116	87		
*	Nyad ctg	A	45 g/m² PP Nonwoven	0.041	18	17	65	6.7	20.8	887	50	70	74		
*	C47972	A	Cellulosic Paper	0.021	12	32	-	-	6.7	5600	98	198	84		

* Cells cycled using constant current discharge (CCD). To compare results to other tests using constant load (resistance) discharge (CLD), use the relationship: CLD = 1.80(CCD) based on cycles to < 1 volt at end of discharge.

[1] All tests done at NASA using NASA Screening Test Procedures.

[2] Nickel-zinc cells - 8-hour cycle - 50% DOD - c/4 Discharge Rate.

[3] S = Solvent-based coating.

[4] Extra yardage run for wheel chair application.

[5] A = Aqueous-based coating.

[6] Mean value normalized to constant load discharge (CLD).

FIGURE 3

COATING SURFACE CRACKS

K 168 ON BTA

Magnification X50

Test results on the pilot and production coated samples are given in Table XI. Inspection of volume resistivity data shows that the original NASA solvent coatings, K19W1 and K158, have higher resistivities than the modified solvent and aqueous coatings developed for pilot and production trials.

The cycle life data in Table XI includes two different types of discharge. Those data preceded by an asterisk (*) were obtained using a constant current discharge. The other data was obtained by discharge through a constant load resistor. This mixture of test data resulted from a replacement of the NASA cell cycle test facilities in October, 1980.

Constant current discharge places greater stress on the cells due to higher sustained current density which results in shortened cycle life when compared to the method of discharge through a constant load resistor where both voltage and current decrease as cell capacity diminishes.

Based on results of three sets of cells cycled by both methods, the relationship of cycle life obtained under constant current discharge (CCD) and constant load discharge (CLD) is given by: $CLD = (1.80 \pm 0.12)CCD$.

To compare data in Table XI, multiply the average of the 3 cycles (CCD) by 1.80 to estimate the cycles under constant load discharge. (Some cycle data was dropped in computing averages; a value was considered an outlier when the standard deviation of the 3 values was 1.5 times the difference between the mean of two values and three values). Once this conversion is made, comparisons can be made with the NASA standard, K19W1 (the first line in Table XI).

On all three substrates, the K177TP coating was definitely superior to K19W1 with respect to resistivity, and gave 25% better cycle life. The extra yardage run of K168P on BTA for the wheel chair battery demonstration cells had low resistivity, very low zincate diffusivity, and gave an average of 222 cycles under a constant current discharge regime and an estimate to 400 cycles when compared to the NASA standard. The K168P formula was modified with Arkon resin.

Some of the solvent coatings in Table XI were cycle tested in 8 ampere-hr Ag/Zn cells. The K177TP on BTA and K168P on BTA achieved 107 and 100 cycles respectively at 50% DOD under constant current discharge. The solvent-coated polypropylene shorted before 50 cycles, regardless of coating. The best

cycle life in Ag/Zn cells (340 cycles at 50% DOD) was obtained from the aqueous K158 formula based on the butyl rubber on a BTA substrate prepared as handsheets. The original solvent standards, X40 and X47W1, (formulations shown in Table V) gave an average of 206 and 233 cycle respectively at 50% DOD under constant load discharge (see Table IV, reference 8).

III. Aqueous Variations of NASA Coatings

One of the major objectives of the program was development of aqueous analogs of selected NASA formulations to eliminate organic solvent use. The relatively heavy coatings specified (i.e., 120 g/m^2 dry) for the solvent base I/O type separator made the quantity of solvents to be evaporated very high. Elimination of solvents greatly reduces health and fire hazards, and substantially reduces the costs.

The same coatings chosen for solvent coating work (cf. Table V) were tried in water-based systems. All of the various pigments utilized in the solvent formulations were readily dispersed in water, using conventional dispersants. Different binders were required since neither Kraton G nor PPO were available in emulsion form. The most promising elastomeric binder which was commercially available in emulsion form was judged to be butyl rubber. It is available as a 60% solids emulsion, BL-100, from Burke-Palmason Chemical Company. The butyl rubber latex did contain some isoprene copolymerized with isobutylene, which did introduce some unsaturation and thus some oxidizable groups. Nevertheless, butyl rubber was more oxidation resistant than all of the larger volume elastomers which were made with high percentages of butadiene or other dienes. Generally, the butyl latex solids used were kept in the same pigment-to-binder ratio as the Kraton or PPO in the original solvent systems.

The butyl latex-bound coatings almost always produced lower resistivity than similar solvent coatings. Also, much higher solids content was possible in the aqueous coatings because the viscosity of polymers in solution is not a factor in emulsion systems. Problems with the butyl latex formulations as compared to solvent systems were their tendency to foam and the softness and flow characteristics of the specific butyl polymer. The softness and flow of the butyl polymer led to "blocking," which is a tendency to stick to adjacent surfaces. Sheets coated with the aqueous coatings generally required a release liner to prevent damage to the coating after being in contact with other sheets as in a roll or a stack of sheets. Other elastomers based on ethylene propylene rubber did not have a high tendency to block, but these were only development products in emulsion form, and expensive for this reason.

Each of the four coatings given in Table V was submitted in aqueous modifications applied to handsheets of PPO and butyl latex treated asbestos, 50:50 SWP: asbestos, nonwoven polypropylene, and saturated wood pulp. The standard separator evaluation test results and cell cycle data for these coated handsheets are tabulated in Table XII. For each coating evaluated, the resistivity was highest for the PPO impregnated asbestos and the polypropylene substrates. The BTA and wood pulp substrates generally showed the lowest resistivities. Electrolyte retention in each coating group was the highest for the wood pulp substrate. Cycle life cell testing was best for the BTA substrate followed by the wood pulp and polypropylene substrates. The results were sufficiently promising to warrant pilot coating work. The 50:50 SWP: asbestos substrate led to explosions in sealed cells and further work was dropped.

It was readily apparent from coated handsheets that formulations made with Plastolein provided lower resistance than Paraplex formulations. For this reason a Plastolein formulation, K40, was chosen for a pilot production study. The pigment dispersion was prepared with 0.2 parts of Tamol 731 dispersant, which allowed use of higher coating solids. The ingredients of the pigment dispersion were mixed in the order listed in Table XIII, and then run through the Gaulin homogenizer at 6000 psi (41.3 MPa) to produce a smooth dispersion. This dispersion was then mixed with the butyl latex binder.

The initial coating trial with aqueous K-40 was made on the BTA substrate. It was found that the reverse roll coating method is the best technique for applying the aqueous coating on an absorbent substrate such as asbestos without excessive penetration into the substrate. The target coat weight of 60 g/m^2 per coat was achieved with good coverage. In addition, a release liner was required to prevent blocking in a coated roll of the K-40 system.

As stated, a release liner is required with this formulation. Along with the butyl rubber, the Plastolein and Paraplex promote blocking. Because in production it would be desirable not to use a release liner, hydrolyzable materials other than the Plastoleins were studied. The study showed that polyacrylate emulsions with relatively high glass transition temperature greatly reduced the tackiness of butyl-bound coatings. In addition, these polyacrylate latexes were found to be extremely effective in producing low electrical resistance (Ref. 9). As with low molecular weight plasticizers, the separators had to be heated in electrolyte to

TABLE XII. STANDARD SEPARATOR TESTS
WATER-BASE HANDSHEET SAMPLES[1]

Coating	Substrate	Dry Thickness cm	Bubble Pressure kPa	Porosity %	Pore Radius Å	Zinc Dendrite Rate cm/min (X 10^4)	Volume Resistivity Ω cm	Cycles to <1 Volt Cutoff Point[2]		
K19W1	PPO Asbestos	.033	48	50	584	-	26.8	315	155	208
K19W1	BTA	.023	159	50	662	8.2	25.7	130	310	300
K19W1	Polypropylene	.028	38	27	502	15.5	63.1	-	190	180
K19W1	50:50SWP:Asbestos	.025	-	66	1879	12.7	28.0	Blew up	320	320
K19W1	Wood Pulp	.036	45	65	1563	11.6	9.2	>210	>210	175
K19W2	PPO Asbestos	.033	117	59	342	12.9	58.3	325	208	360
K19W2	BTA	.023	110	63	258	10.4	22.4	137	118	117
K19W2	Polypropylene	.027	38	32	329	16.7	80.1	>210	190	180
K19W2	50:50SWP:Asbestos	.027	83	53	260	14.1	40.4	251	281	281
K19W2	Wood Pulp	.033	45	49	10426	11.8	24.8	177	190	>210
X40	PPO Asbestos	.031	117	59	572	8.0	20.7	133	104	>350
X40	BTA	.020	90	63	1179	7.6	10.9	>350	266	268
X40	Polypropylene	.025	28	37	2444	18.9	22.3	-	-	-
X40	50:50SWP:Asbestos	.027	55	60	754	-	21.7	Blew up	125	114
X40	Wood Pulp	.032	28	43	4669	12.0	5.6	-	-	-
X47	PPO Asbestos	.030	28	69	4244	-	25.1	-	-	-
X47	BTA	.019	31	56	419	6.9	10.6	-	-	-
X47	Polypropylene	.024	21	35	747	15.1	17.4	-	-	-
X47	50:50SWP:Asbestos	.025	24	58	417	12.8	13.6	-	-	-

[1] All tests done at NASA using NASA Screening Test Procedures.

[2] Nickel-zinc cells - 8-hour cycle - 50% DOD - C/4 Discharge Rate - Constant Load Discharge.

TABLE XIII. FORMULATION OF K-40 COATING

		Dry Parts
Pigment Dispersion:	Cab-O-Sil M5	4.8
	Water to 60% T.S.	
	Tamol 731	0.294
	Calcium Zirconate	142
	Plastolein 9750	47
Coating:	Pigment Dispersion	194.1
	BL-100 Butyl Latex	47

hydrolyze the polyacrylate before the low resistance developed. The polyacrylic acid salts which formed during hydrolysis remain distributed through the coating film, unlike polyacrylic acid salts added to the wet coatings. Polyacrylic acid salts added to butyl latex formulations would be expected to remain in the water phase during film formation, and thus be poorly distributed in the coating. Polyacrylate esters, on the other hand, are much more compatible with butyl rubber than with water and remain intimately mixed in the coating, while polyacrylate salts concentrate in the water phase during drying and finally form aggregates separate from the butyl rubber. To reduce the electrical resistance of barrier coatings, conductive paths must extend completely through the coating. This was achieved with the polyacrylate emulsions.

The use of polyacrylate emulsion in place of the Plastolein in K-40 did not completely eliminate blocking tendency of the coating. For best results, a release liner wound in the production rolls is still required. Further improvement in the blocking tendency was obtained by replacing a portion of the BL-100 binder with an ethylene ionomer resin in combination with a very soft polyacrylate. The latter was used to control a tendency of the coating to crack along sharp folds when formulated with the ionomer. A typical system of this type, K40C, was applied on a 24-inch coater. The recipe is given in Table XIV. Sheets coated with K40C were much improved in block resistance, and had very low volume resistivities. Values of 8 ohm cm were achieved.

Coating work on the 24-inch coater was also done using a then commercially available asbestos sheet, Mannitemp 111, made with some glass fibers and acrylic binder. The asbestos was an electrical grade fiber. Using the K40C formulation, this substrate was successfully coated. The first coat was applied by a nip-fed reverse roll technique and the second coat applied by the rod-coating method. The coated material made this way was sampled to NASA as KFF40C (D-1850-130H). It performed satisfactorily in cell tests. (See Table XI, K40C on Mannitemp 111). This separator exhibited cycle life equivalent to the original solvent base K19W1 made by NASA. It had a much lower resistivity than K19W1.

All of the coating work on asbestos was restricted to the 14-inch or 24-inch machines, where the potential hazard with asbestos was limited to a carefully controlled area. Concurrently, saturated cellulosic paper and nonwoven polypropylene materials were run on a large 65-inch production coater.

TABLE XIV. FORMULATION OF K-40C COATING

		Dry Parts	
Pigment Dispersion:	Water to 65%		
	Tamol 731	0.2	
	Cab-O-Sil M5	3.3	
	Calcium Zirconate	96.5	
Coating:	Pigment Dispersion	147.1	
	BL-100	42.3	
	Rhoplex B15	4.7	
	NH_4OH (28%)	5	Wet
	Surlyn 56230	4.7	

Type S-47971 (Table III) a saturated cellulosic paper, was used as a suitable base for aqueous butyl latex barrier coat ings. Four formulations were applied -- all by rod coating (cf. Table XV), and the coated sheets coded with C-numbers as listed in the table. Each of these coatings behaved satisfactorily on the coater. Coat weights close to the target of 60 g/m^2 per coat were obtained. Spreading and drying were satisfactory, but again a release liner is required to control blocking in finished rolls of separator material. Results of cycle life tests for C-47972 are shown in Table XI.

The first attempt to coat wettable polypropylene on the large production machinery was not successful. The problem was coating penetration and draw control. The latter caused coating cracks because of the stretchable nature of the polypropylene substrate. On a repeat trial the coating viscosity was raised and the coating penetration was successfully controlled. C-49146 and C-49145 were made from 30 and 45 g/m^2 polypropylene webs respectively, with the higher viscosity coating. Fine cracks running the cross-machine direction were formed caused by tensile stresses transmitted to the coating by the forces pulling the web through the coater. These can be corrected by finer tension controls on the coater or by using a carrier belt through the dryer. The latter has been successfully demonstrated on the smaller 14-inch coater.

The effectiveness of Kraton G as a binder in solvent coatings with no blocking problems would make it an attractive binder for aqueous coating if it were available in emulsion form. As Kraton was not available as an emulsion, a program to prepare a useful emulsion from dry Kraton was established as an alternative to the blocking problem of butyl rubber latex or the high cost of the ethylene-propylene rubber latex. By dissolving the Kraton in a minimum of toluene and emulsifying the solution, stable emulsions were developed. Because Kraton emulsions were found not to coalesce well on drying, a combination of equal parts of Kraton G and a saturated alicyclic hydrocarbon resin, Arkon P-85, was used. This combination has excellent oxidation resistance while providing improved pigment binding ability. Substitution of this plasticized Kraton (Table XVI) for butyl rubber virtually eliminated blocking problems, while the electrical resistance of the coatings remained equivalent.

TABLE XV. AQUEOUS COATINGS ON SATURATED PAPER [1]

		C-47973	C-47984	C-47971	C-47972
BL-100		47	47	50	50
Rhoplex HA-16		-	5	-	10
Pigment Dispersion	Calcium Zirconate	142	142	-	-
	Cab-O-Sil M-5	4.8	4.8	-	-
	Tamol 731	0.29	0.29	1.0	1.0
	Plastolein 9750	47	-	-	-
	Nyad 400	-	-	100	100
Total solids of coating (%)		60.4	63.6	61.0	59.8

[1] Formulations expressed in dry parts by weight.

TABLE XVI. KRATON EMULSION

		Dry	Wet
Part A:	Kraton G1650	100	100
	Arkon P-85	100	100
	Toluene	200	200
	Igepal CO-887	4	5.7

After Part A has been dissolved to a homogeneous solution, the water was added slowly while the viscous solution was stirred vigorously by an Eppenbach Homo-Mixer.

Water to 30% active		251
Elvanol 71-30 (10%)	1	10

Aqueous K172 pigment systems with the Kraton emulsion (Table XVII) were applied to nonwoven polypropylene and to BTA. A similar coating containing only wollastonite pigment was applied to a saturated cellulose sheet and to nonwoven polypropylene. In this application the 14-inch coater was used in the same manner as previous aqueous coating. Some colloidal instability was observed during this series of runs and further development will be required to assure running of this system on a large coater. Yardage from these runs was sampled to NASA in March, 1980. Results of cycle tests of aqueous K172 on BTA and 45 g/m^2 PP are given in Table XI. The low cost formulation containing the wollastonite filler is shown in Table XI as Nyad on cellulosic paper and the PP substrates. Only the aqueous K172 on BTA (estimated 245 cycles) is comparable to the original K19W1 standard in terms of cycle life.

IV. Separator Evaluation in Nickel-Cadmium Cells

Some materials developed under this contract were evaluated as separators in nickel-cadmium (Ni/Cd) cells.

The K143B and K143C formulas shown in Table VIII were developed for Ni/Cd evaluation. These coatings were applied to a Kimberly-Clark nonwoven polypropylene substrate. The separators had low resistivity and low bubble pressure. However, after about 600 cycles of testing, the end of charge voltage was increasing (>1.6 volts) and end of discharge voltage dropped below one volt. The tests were terminated. This is contrasted to tests run on the coating base for the above, a Kimberly-Clark 45 g/m^2 nonwoven polypropylene (S-49024) treated for permanent wettability which was successfully tested in sub-C size (one ampere-hour) Ni/Cd cells. In the latter case, six cells have been on test since May, 1980. The test regime is a 1.5 hour cycle; one hour of charge, 0.5 hour discharge. Depth of discharge is 25%. Overcharge is limited to 20%. These cells have completed more than 6000 cycles. Performance is similar to other commercial nylon and polypropylene separators used by Ni/Cd cell manufacturers.

V. Cost Considerations

A final goal of this contract was to demonstrate commercial production feasibility at a cost that would provide a price which would be attractive to large volume battery production. Prices of the widely different designs are dependent on type formulation, solvent versus aqueous, type substrate, in addition to volume and profit required.

TABLE XVII. AQUEOUS KRATON COATINGS[1]

K172	Pigment Dispersion:	Water to 55% T.S.	
		Potassium Salt of Gulf PA-18	1
		Calcium Zirconium Silicate	116.3
		P-25 TiO_2	20
		Elvanol 71-30	5
	Coating:	Pigment Dispersion	142.3
		Strodex PK90	0.5
		50:50 Kraton G1650:	
		Arkon P-85 Emulsion	40
		Plastolein 9750 (pre-emulsified)	16
Low-Cost Pigment Formulation			
	Pigment Dispersion:	Water to 60% T.S.	
		Potassium Salt of Gulf PA-18	1
		Nyad 400 (Calcium Silicate)	100
		Elvanol 71-30	5
	Coating:	Pigment Dispersion	200
		50:50 Kraton G1650:	
		Arkon P-85 Emulsion	100
		Strodex PK90	0.525

[1] Formulations expressed as dry parts by weight.

Typical price levels for a barrier-coated product on a polypropylene or cellulose substrate would be as follows:

	Price, $ per Square Yard[1]
Aqueous Designs	1.20 - 1.65
Solvent Designs	1.45 - 1.90

[1] Based on 1981 raw material and production costs for 100,000 square yard amounts.

Prices for the same designs on a fuel cell grade asbestos design would be significantly higher due to the limited availability of this type asbestos as well as undetermined additional costs of processing environmentally unacceptable asbestos. Use of fuel cell grade asbestos would be expected to add over $1.25 per square yard for raw material alone to the above prices.

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As a final note to further aid the reader, the authors have requested NASA to provide comparative results on other separators evaluated in nickel-zinc batteries. This information is summarized in Appendix B.

SUMMARY OF RESULTS AND CONCLUSIONS

The work to produce improved versions of the NASA inorganic-organic (I/O) separator materials and make commercial preparations was moderately successful.

A single-ply asbestos substrate was made, eliminating separation along ply lines. The beater-treated asbestos sheet (BTA) has practical application as a coating base. In this case, a stronger substrate is desired and this should be achieve with the use of virgin fiber. Two alternative coating base substrates have also been demonstrated to have application; one a saturated cellulosic sheet and the other a nonwoven polypropylene web treated for wettability.

Solvent coatings developed at NASA and modified by Kimberly-Clark have been applied to each of the above substrates on a small production coater in spite of the tendency to develop cracks. The cracks result from the fast removal of the solvent in the dryer even at ambient temperatures. The control coating, K19W1, was less prone to crack than the newer NASA formulations, but had an undesirably high resistance. The newer formulations contained very fine particle size fillers close to the pigment volume content of earlier NASA coatings which used larger particle size fillers. The tendency to develop micro-cracks on drying is an indication of inadequate binder to form strong films.

Aqueous coatings patterned after the solvent-based formulations were developed using butyl latex as the binder. These coatings were applied at high solids and offered substantial cost reduction over the solvent coatings. A release liner will be necessary with the manufacture of these barrier separators. The butyl latex has an inherent tackiness. Problems with coating flaws caused by foam are controlled by use of multiple coatings. The use of polyacrylate polymer additives in place of Plastolein provided improved low electrical resistance with substantially less blocking. It must be emphasized that the blocking is inherent to the nature of the binder. The use of ethylene-propylene rubber latex eliminates the blocking difficulty, but application of butyl latex is prompted by economic considerations.

The solvent coatings bound by Kraton thermoplastic elastomer do not block. The development of a Kraton emulsion system was successful. Some colloidal problems were experienced with these Kraton emulsion coatings, mostly the result of the low molecular weight Plastolein. While no production runs were made with the latest improvements in the coating formulations bound by Kraton, they are believed to be coatable.

Several commercially prepared solvent-base coated asbestos separators exhibited better performance and cycle life than the K19W1 standard as test by NASA. Cellulose and nonwoven polypropylene as a replacement for asbestos showed little or no improvement in cycle life; nevertheless nonwoven polypropylene, a permanently wettable Kimberly-Clark product showed cell lives in excess of 6,000 cycles when used as an absorber in nickel-cadmium cells. The water-based coatings showed acceptable separator properties on the three substrates, but the cycle life was not improved over the solvent coating systems.

From the standpoint of producing a commercial product, the use of asbestos is unacceptable. The use of toluene solvent is both expensive and environmentally unacceptable without proper solvent recovery equipment. Although water-based coatings on cellulose paper or polypropylene webs are acceptable from the production standpoint, they do not represent an improvement over solvent-base coatings.

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A P P E N D I X

APPENDIX A

NASA Procedure

DETAILS OF Ni/Zn SEPARATOR EVALUATION TESTS

The separator materials were evaluated in 7.2 ampere-hour nickel-zinc (Ni/Zn) cells. The cells contained a negative to positive ratio of about 3 to 1. The cells contained 4 Ni electrodes and 2 Zn electrodes with a + - ++ - + configuration; that is, a double positive electrode in the middle. The electrode dimensions were 7.3 cm x 9.4 cm (68.6 cm^2). The Ni electrodes were bagged in uncoated asbestos while the Zn electrodes were bagged in the trial separator with coated side out. The cycle regime was a 50% DOD test (8 hours - 6 hours charge - 1.9 hours discharge) 3 cycles per day. Once per day an 18 minute open circuit stand occurred. The amount of overcharge was limited to less than 5%. The electrolyte level was maintained near 1/2" from the top of the separator bags. The cells were initially sealed. The seal was broken only if electrolyte or water was added. The electrolyte used was 35 weight percent KOH.

The charge-discharge was performed through a set resistance which once adjusted to provide proper values (1.8 amps discharge, 0.63 amp charge) was not changed. The separator on the Zn electrode with asbestos on the Ni electrode would reach 1.90-1.92 V at the end of charge. One volt was used as the cutoff voltage on discharge. When the one volt value was reached, the cells were removed from the test rig, the capacity remained was determined, and the cell recharged.

Procedure:
Dip each edge of the half-bags into an acrylic-acetone solution. This procedure is repeated 5 times per edge. For 5% Kraton in Toluene, only 1 dip is required. Depth of Application is such as to form an untreated "window" slightly larger than the electrode which is later to be placed between 2 half-bags. The wet product edges are allowed to dry upon a pedestal of some sort in contact with the center, undipped portion.

Put the dry edge-dipped product, non-coated surface face up, upon a clean sheet of paper. Position an electrode on the surface so that its sides are equidistant from the edges. The bottom margin of the electrode should lie more than 1/4 inch from the lower edge.

Cut a strip of 1/8 inch thick, 1/4 inch wide foam tape from its roll. The cut sample should be somewhat longer than the sum of

3 sides of the separator (2 long, plus 1 short side). Place the foam, sticky surface down, upon a piece of Teflon. Position a short side of some object identical in shape and dimension to that of the half-bag against the tape, so that the tape to either side of the object is longer than one long side of the latter. Mark the 2 points at which the object touches the tape, lift the tape from the Teflon and cut "V" shapes out of the tape so that their splices lie about 1/4 of the way into the tape on the spots formerly occupied by the marks. Now position the tape, sticky surface down, along 2 long and 1 short margins of the separator in such a way as to allow the electrode to fit snugly as to make it impossible to move the electrode in or out of the "margined" half-bag. This operation is best performed by first laying the tape down upon one short edge of the bag, each "V" cut-out lying on its respective separator corner, then bending the tape around one corner and along a separator long margin. The bending and positioning along the second long margin then follows. In each instance, some pressure should be applied against the release sheet surmounting the tape, thus enabling the sticky-down surface to adhere to the separator margin.

Push the electrode against the tape running along the short margin, pull the release sheet from its upper surface and place a second half-bag, non-coated side face down, over the original one so that the edges of each are super-imposed one upon the other as perfectly as is possible. Press down upon the margins of the second half-bag so that they adhere to the foam. Place a ribbon of thin tissue paper on top of the exposed foam surface and press down to make it adhere. Cut away most of the excess quadrille paper.

CONSTRUCTION OF SEPARATOR BAGS FOR ALKALINE CELLS

Materials Required:

Acrylic-acetone solution for Ag/Zn cells (PPO based separator)

5% Kraton G-1650 solution in Toluene for Ni/Zn cells (Kraton based separator)

Asbestos separator pieces (half-bags)

Pedestals

Electrodes

Quadrille paper

Polyethylene foam tape (1/8" thick x 1/4" wide)

Scissors

Razor blade

Teflon sheet (approximately 4" x 14")

Teflon sheet (half-bag size)

Marker, black or red

Tissue paper (approximately 3/8" x 5")

Flat, heatable surfaces (at least 6" x 10")

7 lb. weights (approximately)

Constant temperature oven

APPENDIX B

Comparative Tests of Other Separator Materials

At the request of Kimberly-Clark, the information in this appendix was provided by NASA so the reader would have some comparative results on other separators which have been evaluated in Ni/Zn batteries by NASA. The results should aid in putting the materials of this report into perspective.

Figure B-1 shows results of cycle life tests of various commercial and developmental materials which were available from 1976 through 1980. The data is normalized to reflect constant load discharge as discussed on page 27. The construction details of the test cells are described in Table B-I. The results show that the Kimberly-Clark commercially prepared materials are for the most part at least equivalent in cycle life to other separator concepts. The Kimberly-Clark commercially prepared materials are between the K19W1 NASA standard and the NASA K143 separators. The latter represented an advance in the NASA I/O separator. The K177TP on cellulose paper and polypropylene appear to be an improvement over commercial materials and on a par with K19W1 with regard to cycle life.

Figure B-2 is included to provide the reader with an example of comparative performance data on three separators; the K19W1 standard, the Kimberly-Clark water base KN40A on cellulose paper substrate, and a state of the art design consisting of 3 dual layers of cellophane-Celgard. The latter combination was developed for the Air Force for a remote pilotless vehicle (RPV) application. These separators were evaluated in 300 Ampere-hour nickel-zinc cells built for evaluation in electric vehicles. The voltage vs amp-hr capacity curves show the improvement in resistivity of the KN40A when compared with the K19W1. The midpoint voltage (at 150 amp-hr) of KN40A is 120 millivolts higher than the K19W1, and is equivalent to the combination of commercially available products.

FIGURE B-1

CYCLE LIFE COMPARISONS
OF COMMERCIAL & DEVELOPMENTAL MATERIALS,
KIMBERLY-CLARK PRODUCTION RUNS WITH
NASA PRODUCTION BATCHES

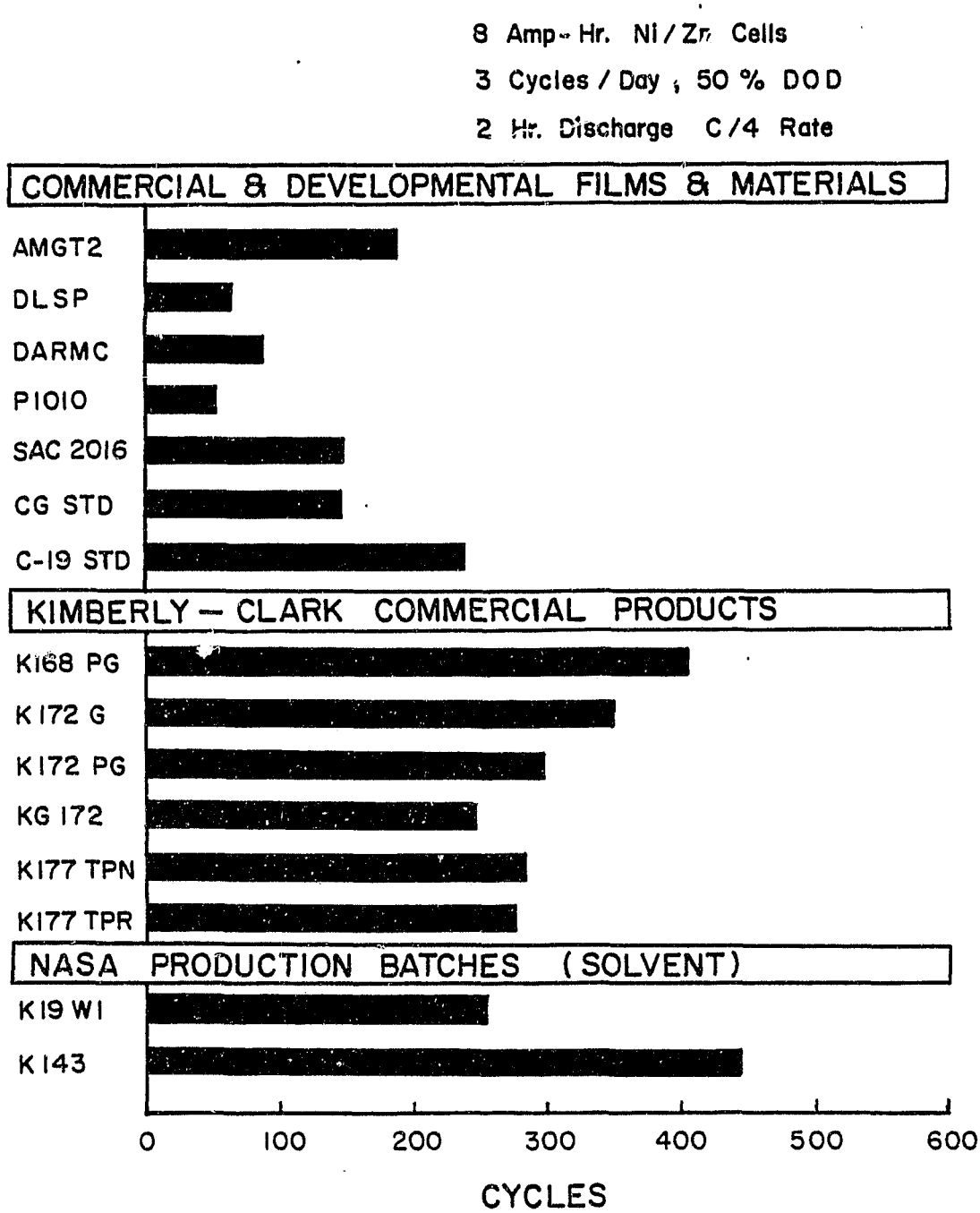

TABLE B-1

Ni/Zn Cell Construction (Figure B-1)

Material	Ni Electrode	Zn Electrode	Supplier
AMGT2	BTA	AMGT2 (10 mils)	Amerace Corporation
DLSP	BTA	DALKASEP (1 layer)	W. R. Grace
DARMC	BTA	DURAMIC (1 layer)	W. R. Grace
P1010	BTA	P1010 (2 wraps)	RAI
SAC 2016	BTA	EATH 2016 (2 wraps)	SAC Membrance Products
CG STD	BTA	Celgard 3400 (2 wraps)	Celanese Research
C-19 STD	Pellon (5 mil)	Cellophane (5 wraps)	Yardney Electric
K168 PG	BTA	K168 (solvent) on BTA	Kimberly-Clark
K172 G	BTA	K172 (solvent) on BTA	Kimberly-Clark
K172 PG	BTA	K172 P (solvent) on BTA	Kimberly-Clark
KG 172	BTA	K172 (aqueous) on BTA	Kimberly-Clark
K177 TPN	BTA	K177 TP (solvent) on cellulose	Kimberly-Clark
K177 TPR	BTA	K177 TP (solvent) on polypropylene (S-49024)	Kimberly-Clark
K19 W1	Asbestos (2% PPO)	K19 W1 (solvent) on asbestos (2% PPO)	NASA
K143	Asbestos (2% PPO)	K143 (solvent) on asbestos (2% PPO)	NASA

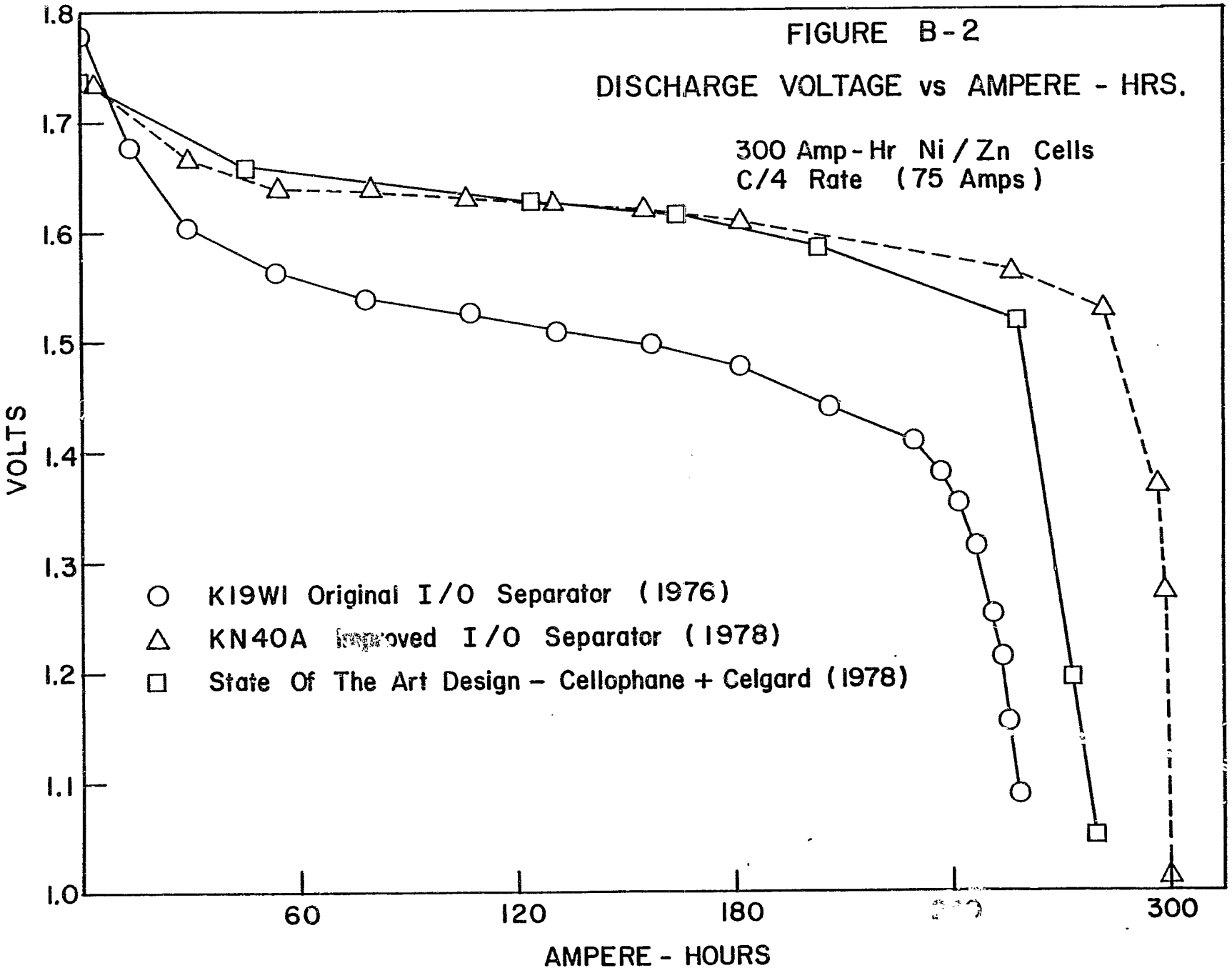
FIGURE B-2
DISCHARGE VOLTAGE vs AMPERE - HRS.
300 Amp-Hr Ni / Zn Cells
C/4 Rate (75 Amps)
K19WI Original I/O Separator (1976)
KN40A Improved I/O Separator (1978)
State Of The Art Design – Cellophane + Celgard (1978)
VOLTS
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
60
120
180
300
AMPERE - HOURS